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SYNTHESIS AND HOT PRESSING OF ZnS POWDERS

by

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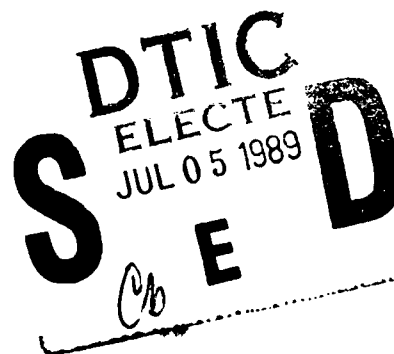
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Synthesis and Hot Pressing of ZnS Powders

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ABSTRACT

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→ Zinc sulfide powders with submicron particle size were prepared by homogeneous precipitation from acidic zinc solutions by aging with thioacetamide at elevated temperatures. Monosize, polycrystalline particles having 0.35 μm diameter were obtained. Sulfide ion generation rate in solution depended on temperature, pH and initial thioacetamide concentration. The rate of sulfide ion generation, in turn, influenced precipitation kinetics and particle morphology. The types of supporting anions in solution also influenced the morphology of the particles produced.

Monosize powders were hot pressed for various time, temperature and pressure combinations. Compacts achieved near-theoretical density in less than 30 minutes at temperatures 850-900°C and applied pressures of about 70-105 MPa. The dominant densification mechanisms were identified at various stages of the process.

1. INTRODUCTION

The fabrication of ZnS for IR transmitting windows has been studied by a number of investigators. The majority of the work involved either hot pressing of poorly characterized powders (1) or chemical vapor deposition of ZnS onto cold substrates (2). Generally, hot pressed samples displayed nonuniform microstructures, with a relatively large average grain size probably due to the large average particle size of the starting powders. Similarly, CVD materials exhibited large grain size and an anisotropic microstructure due, in part, to the unidirectional growth pattern of the technique itself. The first prerequisite for obtaining small and uniform-grained microstructures by hot pressing is to employ powders that exhibit a narrow size distribution and a small ($\bar{D} < 1 \mu\text{m}$) average particle size.

The synthesis of colloidal ZnS particles has been investigated previously. Chin (3) was the first to prepare uniform, spherical ZnS particles from very dilute zinc solutions ($[\text{Zn}^{++}] < 10^{-3}\text{M}$) by bubbling H_2S in the presence of ethylene diaminetetraacetate. Uniform ZnS spheres with diameters of several micrometer were also synthesized by aging acidic zinc sulfate solutions in the presence of thioacetamide at elevated temperatures (4, 5).

Start → A comprehensive investigation into the processing of ZnS, which involve synthesis and characterization of submicron powders and their processing at elevated temperature to produce dense ceramic parts, was the main objective of this investigation. Thermomechanical characterization of the dense polycrystalline ceramics is also an integral part of such a study, and is underway.

2. POWDER SYNTHESIS AND CHARACTERIZATION

Precipitation of ZnS was carried out by aging acidic zinc solutions in the presence of excess thioacetamide (TAA). When TAA is aged at elevated temperature, it releases H_2S according to the following reaction:



Hydrogen sulfide (H_2S) in turn dissociates stepwise to produce HS^- and S^{2-} ions, the concentrations of which are determined by the appropriate equilibrium constants and the concentration of H_2S at the temperature in question.

Precipitation of ZnS particles occurs when relative supersaturation exceeds a critical value. The relative supersaturation (RS) is defined as:

$$\text{RS} = \left(\frac{[\text{Zn}^{++}][\text{S}^{2-}]_e}{K_{sp}} \right)^{1/2} \quad (2)$$

Where $[Zn^{++}]$ and $[S^{-}]_t$ are the concentrations of zinc and sulfide ions at time t and K_{sp} is the equilibrium solubility product at the temperature in question. The morphology of precipitated ZnS particles is largely determined by the rate at which this critical supersaturation value is approached. Higher approach rates favor small, irregularly shaped and highly agglomerated particle assemblies; whereas, slow approach rates favor uniform and monodisperse particles.

Since the zinc ion concentration is constant and equal to initial zinc salt concentration prior to nucleation, the precipitation kinetics are largely controlled by the sulfide ion generation rate. Concentration of sulfide ion at any time is given by (6):

$$[S^{-}]_t = \frac{[TAA]_0 (1 - \exp(-k[H_3O^{+}]t))}{\frac{[H_3O^{+}]^2}{K_1 K_2} + \frac{[H_3O^{+}]}{K_2} + 1} \quad (3)$$

where $[TAA]_0$ is initial concentration of thioacetamide, $[H_3O^{+}]$ is concentration of hydronium ions, k is the rate constant for decomposition of thioacetamide at the temperature, K_1 and K_2 are equilibrium dissociation constants for H_2S and HS^{-} at the temperature, and t is time.

As Equation (3) indicates, the rate of sulfide ion generation is determined by the initial concentration of TAA, temperature and the acidity of the solution. A large number of experiments with various combinations of these variables were carried out to assess the influence of these individual variables on the precipitation. It was found that the nucleation of ZnS occurs at a critical RS value of about ten, irrespective of the specific values of the individual variables. Furthermore, the time required to reach this critical RS value controls the morphology of the ZnS particles formed. When time-to-nucleation was less than 4 minutes, the powders with bimodal or narrow size distribution were produced. When time-to-nucleation was longer than 4 minutes, spherical monosize particles were obtained. At time-co-nucleation values of about 15 minutes, monosized spherical submicron ZnS particles with near theoretical yields were always obtained, however, yields decreased as time-to-nucleation increased. When the time-to-nucleation exceeded 30 minutes, the yields were relatively low for reasonable aging times i.e. several hours. Figure 1 shows the progression of powder morphology with decreasing time-to-nucleation.

In addition to the influences of temperature and the concentrations of reactants, such as Zn^{++} , H_3O^{+} and TAA, it was found that the type of supporting anion (e.g. SO_4^{2-} , CH_3COO^{-} or Cl^{-}) influenced the precipitation kinetics and the morphology of the particles formed. The morphology of particles obtained under identical conditions except for the type of supporting anion employed is shown in Figure 2. As the figure indicates, particles formed in the presence of nitrate and chloride ions exhibit similar morphology. These particles were monosized having an average diameter of about 0.35 μm , and consisted of only the cubic sphalerite (β -ZnS) phase (Figure 2a and 2b). On the other hand, acetate supported solutions produced monosized spherical but smaller particles ($\bar{\phi} \approx 0.2 \mu m$) and lower yields at comparable aging times. Acetate derived particles also consisted of the sphalerite phase (Figure 2c). Although nucleation occurred much sooner for the acetate than for the nitrate or chloride systems, the growth of particles was much slower. The slower precipitation kinetics observed for the acetate system could not be explained either by simple complexation or buffering phenomena. Particles obtained from sulfate supported solutions were distinctly different in morphology than the others, as is shown in Figure 2d. These particles were about 3 μm in diameter and exhibited a fibrous substructure, especially for long aging times. X-ray diffraction patterns indicated that the fibrous powders consisted of a mixture of wurtzite (α -ZnS) and sphalerite (β -ZnS) phases. The apparent critical RS value for sulfate solutions was found to be higher than for the other supporting anions. However, when complexation of zinc ions with sulfate ions was considered, the actual critical RS value was about ten, similar to that observed for nitrate and chloride containing systems.

3. HOT PRESSING

Monosize (0.35 μm), spherical ZnS powders derived from zinc nitrate solutions were used for hot pressing experiments. The powders were pressed to 0.95 cm diameter pellets first in a double acting steel die, followed by cold isostatic press at 200 MPa. Hot pressing was carried out in a graphite die under flowing nitrogen atmosphere. The influence of hot pressing temperature,

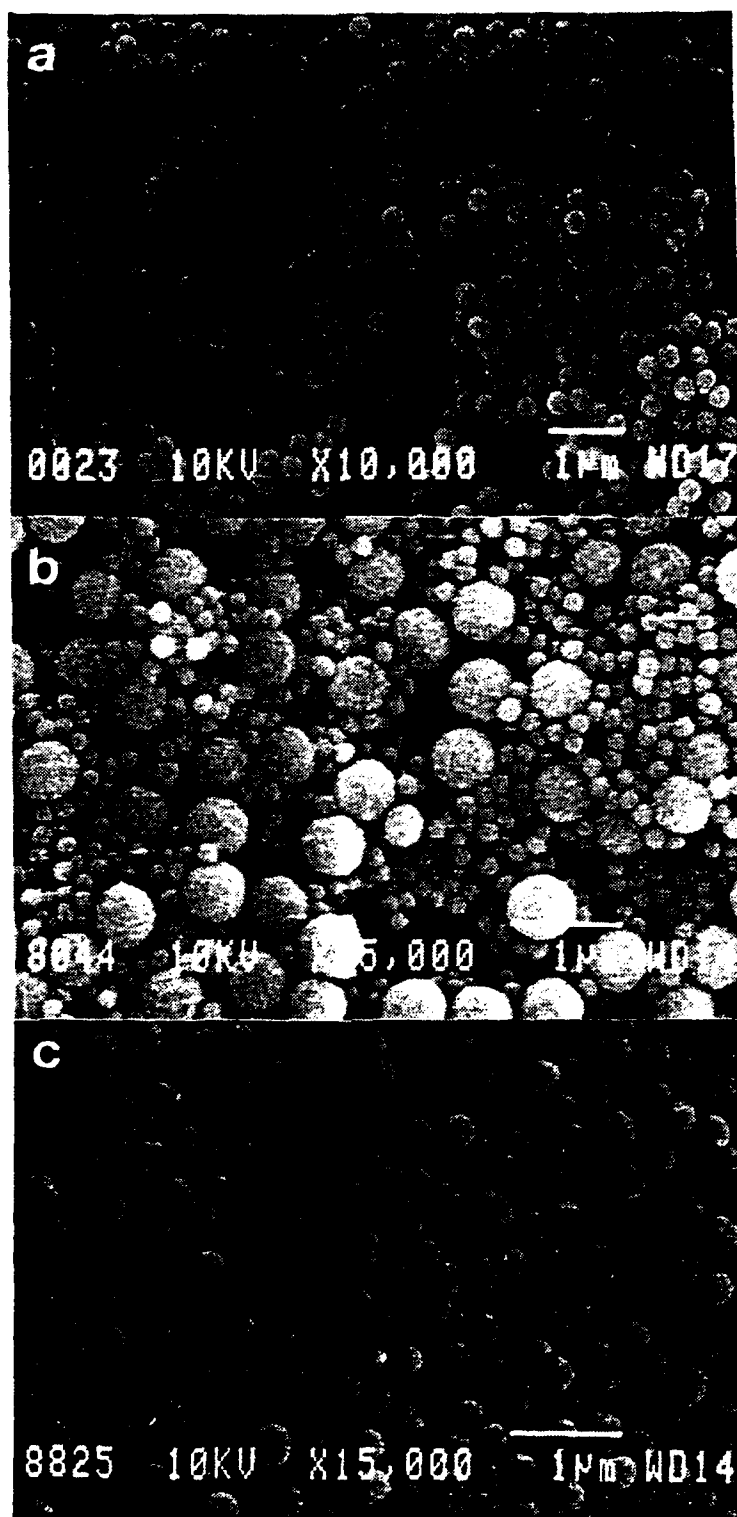


Figure 1. Morphology of the ZnS particles obtained at various time-to-nucleation values. Initial zinc ion concentration was kept constant at 0.05 M $\text{Zn}(\text{NO}_3)_2$, and nitric acid was used to adjust the pH of the solution. Time-to-nucleation a) 70 min. b) 2 min. and c) 0.8 min.

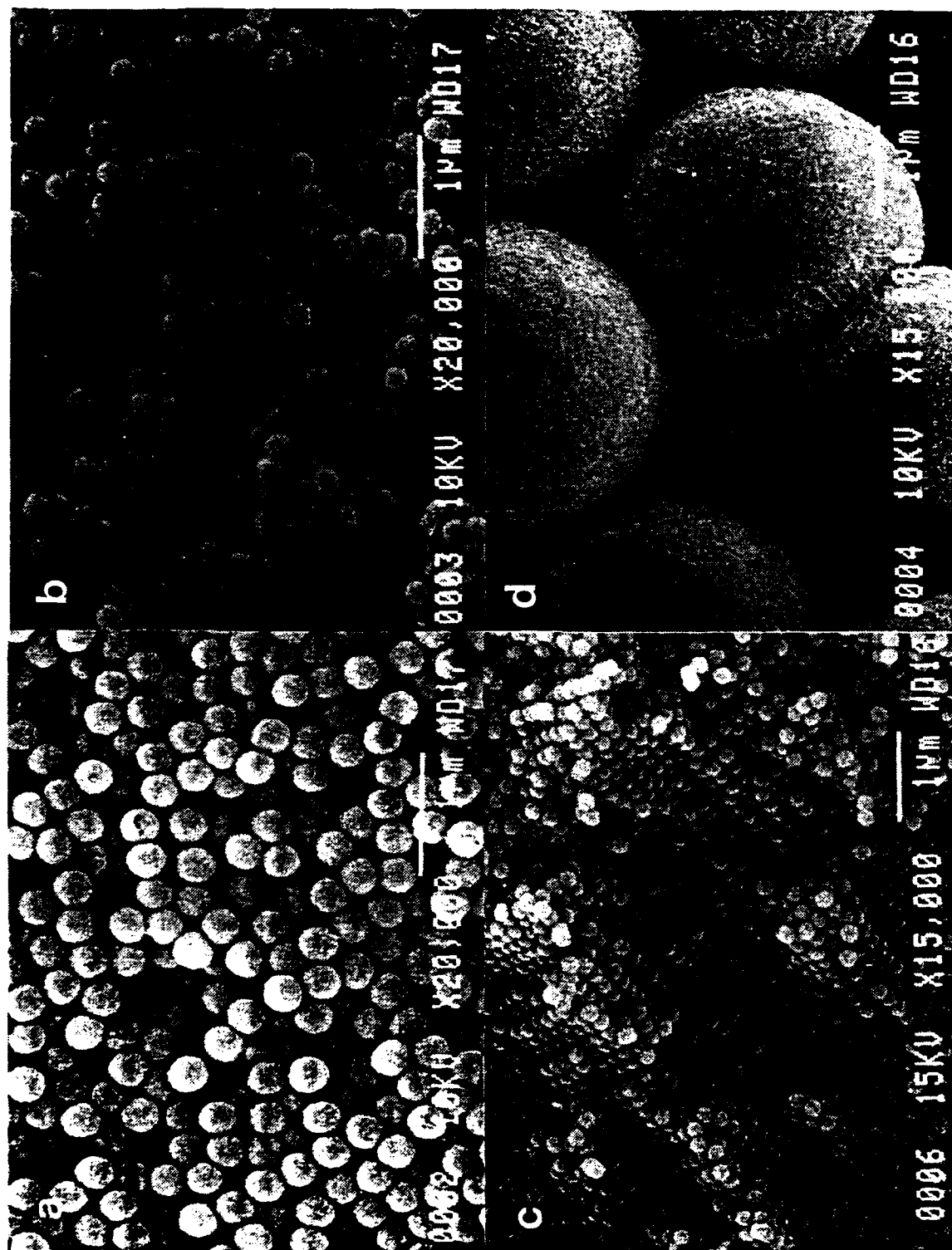


Figure 2. Morphology of the ZnS particles obtained by aging 0.05 M Zn^{++} solution at $T = 70^{\circ}C$, $[TAA]_0 = 0.8M$, $pH = 2$ for $t = 60$ min., using different supporting anions: a) nitrate, b) chloride c) acetate d) sulfate

even at 3 minutes (Figure 4b). Most of the remaining porosity appears to be at the grain boundaries. The pore free condition has been reached in less than 30 minutes for this pressure (Figure 4d); this condition reached much sooner at higher applied pressures. Average grain size for the hot pressed samples was about 0.5 μm . A significant amount of twinning was also observed for samples that were pressed at higher pressures. Pellets that were hot pressed at 900°C and 105 MPa appeared to be translucent.

4. DISCUSSION

Preparation of uniform, spherical submicron size ZnS powders was accomplished by homogeneous precipitation of zinc ions from hot aqueous thioacetamide solutions. Depending on the rate of sulfide ion generation rate, powders having either monosize, bimodal or continuous size distribution were obtained. The spherical particles were found to be polycrystalline, and, with the exception of powders precipitated in the presence of sulfate ions, these powders exhibited only the sphalerite phase. X-ray line broadening and surface area measurements indicate that the crystals making up the particles were about 15 nm in size. The critical nucleus size may be calculated from the Kelvin equation:

$$r^* = \frac{\sigma \bar{V}}{RT \ln(RS)} \quad (4)$$

where σ is the surface tension of ZnS. When the observed critical RS value of 10 is used in this equation, r^* is calculated to be 15 nm. This implies that the actual growth mechanism is by nucleation of 15 nm crystals followed by aggregation of these crystals to form submicron or micron size spherical particles.

The influence of the supporting anion on the growth habit of colloids has long been recognized, thus it is not surprising to see that the growth behavior of particles in the presence of a strong complex former such as sulfate is different than that of non-complexing chloride and nitrate ions. The specific growth mechanism associated with a particular anion, however, was not studied.

Hot pressing studies using monosize powders indicated that these powders could be pressed to full density at much lower pressures than had been previously (7). The hot-pressed compacts exhibited submicron grain size and uniform microstructures. These samples exhibited transgranular fracture, implying strong diffusional bonding between the grains. Using the densification rate expressions developed by Ashby and his coworkers (8), it appears that the grain boundary diffusion mechanism dominates the densification process after an initial period involving grain sliding and deformation of the particles (9). This conclusion is in agreement with the strong grain boundaries observed in fractured samples. Densification maps generated for this system indicated that, after one minute of hot pressing at 850°C or above, the compact entered final stage sintering with boundary diffusion controlling the densification. Higher temperatures influenced the densification rate much more strongly than higher applied pressures. However, the use of higher temperatures and/or longer hot pressing times is limited by the high vapor pressure of ZnS at elevated temperatures.

5. SUMMARY

Uniform, submicron spherical powders consisting 15 nm sphalerite crystals were produced by homogeneous precipitation from aqueous solutions using thioacetamide as the precipitating agent. The morphology, yield and precipitation kinetics were related to sulfide ion generation rate and support anions. Powders with optimum morphology and yield were produced from solutions containing nitrate ions, at 70°C in 90 minutes. The mechanism of particle formation was found to be formation of 15 nm crystalline nuclei followed by aggregation of these nuclei to form submicron, spherical particles.

Hot pressing of these powders at various temperature-pressure-time combinations was studied. At temperatures as low as 850° and at pressures as low as 70 MPa densities greater than 99% theoretical were achieved. These compacts exhibited uniform submicron grain size with strong grain boundary bonding.

pressure and time on the density and on the evolution of microstructure was studied.

The densities of ZnS pellets hot pressed at 900°C for various combinations of time and pressure are given in Table 1 and plotted in Figure 3. Influence of hot pressing temperature on the final density and microstructure is discussed in detail elsewhere (6).

TABLE 1. Densities of ZnS compacts at various time and pressure combinations at 900°C (Sphalerite theoretical density - 4.10 g/cm³)

time min.	Final Density, g/cm ³			
	P = 17.5 MPa	P = 35 MPa	P = 70 MPa	P = 105 MPa
1	3.60	3.87	3.95	3.99
3	3.78	3.90	3.92	4.04
6	3.81	3.93	4.00	4.06
12	3.84	3.94	4.04	4.08
18	3.85	3.98	4.05	4.08
24	3.89	4.00	4.05	4.09
30	3.92	4.01	4.05	4.08
60	--	4.01	4.06	4.08

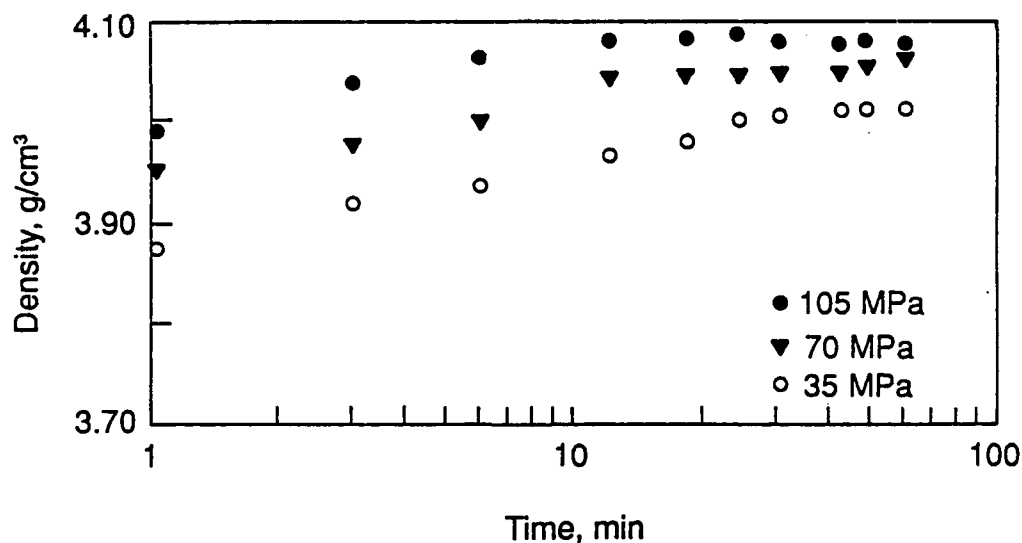


Figure 3. Variation of density with time of ZnS compacts at T = 900°C and at different applied pressures.

Hot pressed densities of ZnS pellets indicate that the influence of applied pressure is much more significant than that of pressing time. Indeed it appears that terminal densities are achieved at 24, 18 and 12 minutes for pressures 35, 70 and 105 MPa respectively. The highest densities obtained for an applied pressure of 105 MPa correspond to >99.5% theoretical.

Microstructures of pellets hot-pressed at 900°C and 17.5 MPa are shown for various times in Figure 4. The micrographs clearly indicate that the final stage of densification is underway

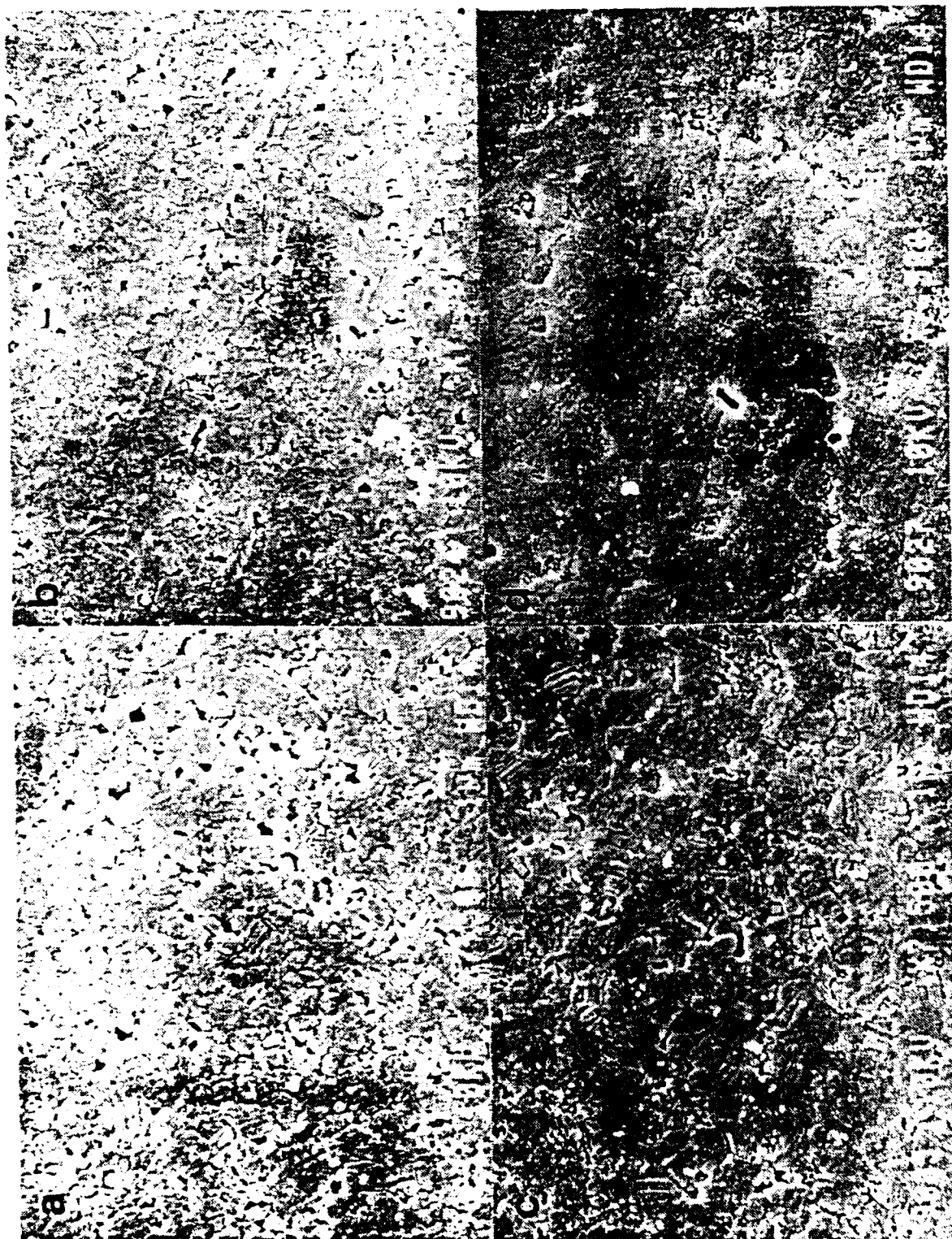


Figure 4. Microstructure of ZnS compact hot pressed at 900°C at P = 17.5 MPa for a) 3 min., b) 12 min., c) 18 min., and d) 30 min.

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